WEST Search History

DATE: Sunday, October 20, 2002

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	DB=USPT; PLUR=YES; OP=ADJ		
L16	((L15) and (anion exchang?$4))	5	L16
L15	l1 with l2 with l12	72	L15
L14	l1 same l2 same l12	237	L14
L13	l1 and l2 and L12	9897	L13
L12	(poly styrene) or (polystyrene)	107963	L12
L11	styrene or polystyrene	184291	L11
L10	((l8) and (l1 with l2))	63	L10
L9	((L8) and (l1 same l2))	71	L9
L8	L7 and l2	94	L8
L7	l1 and L6	119	L7
L6	521/27	790	L6
L5	L4 l1 and l2 and l4	1	L5
L4	(ion or anion) adj (exchang?$4)	72397	L4
L3	(ion or anion) adj (exchang?4)	0	L3
L2	electron or gamma	305398	L2
L1	irradiat?$4	115165	L1

END OF SEARCH HISTORY

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Collections
Definition, Editing, Browsing

Name: Undefined

Contents:

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4169023
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Comment:

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- US Patents Pre-Grant Publication Full-Text Database
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L15: Entry 5 of 72   File: USPT   Oct 23, 2001

DOCUMENT-IDENTIFIER: US 6306646 B1
TITLE: Culture dish

Brief Summary Text (1):
The invention relates to a culture vessel made of plastic for growing cell and tissue cultures according to the preamble of claim 1. Such vessels have been known for a long time for plant and animal cell cultures. In the past, glass bottles and dishes were primarily used. For one-time use, culture vessels made particularly of thermoplastic materials, e.g., polystyrene, have proven successful. Due to their normally hydrophobic surface, such polystyrene vessels are irradiated, for example, with gamma rays. The culture vessel can be, for example, a Petri dish, a multidish or, for example, also a microtiter plate or a microtest plate. Such culture vessels are described, for instance, in the publication by Lindl and J. Bauer, "Zell- und Gewebekultur" [Cell and Tissue Culture], 3rd Edition, Gustav Fischer Verlag (1994).

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L15: Entry 51 of 72　　　　　　　　　File: USPT　　　　　　　　Oct 24, 1989

DOCUMENT-IDENTIFIER: US 4876129 A
TITLE: Packaging material for photographic photosensitive materials

Detailed Description Text (19):
The outer layer is formed of a thermoplastic resin. This thermoplastic resin is
preferably a polyolefin resin, such as LDPE resin, medium-density polyethylene (MDPE)
resin, HDPE resin, L-LDPE resin, ethylene-propylene copolymer resin (random type or
block type), ethylene-(butene-1) copolymer resin, propylene-(butene-1) copolymer resin,
poly (butene-1) resin, polystyrene resin, poly(methyl methacrylate) (resin,
styrene-acrylonitrile copolymer resin, ABS resin, PP resin, crystalline
propylene-.alpha.-olefin copolymer resin, modified polypropylene resin, modified
polyethylene resin, polypropylene-maleic anhydride graft copolymer resin, chlorinated
polyolefin resin such as chlorinated polyethylene resin, chlorinated HDPE resin,
chlorinated LDPE resin, chlorinated polyethylene copolymer resin and chlorinated
atactic PP resin, EVA resin, ethylene ionomer resin (copolymer of ethylene and
unsaturated acid crosslinked by metal ions), poly(4-methylpentene-1) resin,
ethylene-acrylic acid copolymer (EAA) resin, EMA resin, vinyl chloride-propylene resin,
ethylene-vinyl alcohol copolymer resin, crosslinked polyethylene resin (electron rays
irradiation crosslinking, chemical crosslinking, etc.), polyisobutylene resin,
ethylene-vinyl chloride copolymer resin and poly(1,2-butadiene)resin.

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DOCUMENT-IDENTIFIER: US 4775474 A
TITLE: Membranes containing microporous structure

Detailed Description Text (3):
Asymmetric membrane compositions are prepared by irradiating one side of 5 inches by 5
inches square, 51 .mu.m thick polystyrene films (sold commercially as Trycite* 1000
polystyrene film by the Dow chemical Company) using electron beam (EB) radiation (i.e.,
using a CB150/15/10L electrocurtain electron beam processor with 150KV accelerating
voltage). Dosages of electron beam radiation for each sample is provided in Table I.
During irradiation of the films a second layer of 102 .mu.m thick polystyrene film is
placed on top of the first sample. The irradiated samples (i.e., the first films) are
then taken and partially crazed by immersion in n-heptane at 33.5.degree. C. for 170
minutes. The crazed film is dried under vacuum and sectioned for observation under
microscope. The thickness of the dense core layer and its position in the film is
measured (as evidenced by the Asymmetric Ratio which is the ratio of the thickness of
the thicker crazed layer over that of the thinner crazed layer). Data are presented in
Table I.

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L15: Entry 70 of 72   File: USPT   Nov 5, 1974

DOCUMENT-IDENTIFIER: US 3846521 A
TITLE: LOW ENERGY ELECTRON BEAM TREATMENT OF POLYMERIC FILMS, AND APPARATUS THEREFORE

Brief Summary Text (3):
It has been proposed to alter the gas permeability properties of certain types of
polymeric films to a useful degree by various types of radiation treatment. For
instance, Huffman et al., U.S. Pat. No. 3,239,996, disclose the treatment of films made
from tetrafluoroethylene, polyethylene, polypropylene, polystyrene, ethyl cellulose,
and polyethylene terephthalate, with irradiation by X-rays, gamma rays, beta rays, and
particles from a Van de Graaff accelerator. As a result of such treatment, the
usefulness of such films for separating helium from natural gas is enhanced.

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L10: Entry 7 of 63   File: USPT   Aug 22, 2000

DOCUMENT-IDENTIFIER: US 6107422 A
TITLE: Copolymer of an olefin and an unsaturated partially fluorinated functionalized monomer

Brief Summary Text (661):
Because of the relatively large amounts of .omega.,1-enchainment that may be obtained using some of the polymerization catalysts reported herein novel polymers can be made. Among these homopolypropylene (PP). In some of the PP's made herein the structure ##STR79## may be found. In this structure each C.sup.a is a methine carbon atom that is a branch point, while each C.sup.b is a methylene group that is more than 3 carbon atoms removed from any branch point (C.sup.a). Herein methylene groups of the type --C.sup.b H.sub.2 -- are termed .delta.+ (or delta+) methylene groups. Methylene groups of the type --C.sup.d H.sub.2 --, which are exactly the third carbon atom from a branch point, are termed .gamma. (gamma) methylene groups. The NMR signal for the .delta.+ methylene groups occurs at about 29.75 ppm, while the NMR signal for the .gamma. methylene groups appears at about 30.15 ppm. Ratios of these types of methylene groups to each other and the total number of methylene groups in the PP is done by the usual NMR integration techniques.

Brief Summary Text (664):
The above ratios involving .delta.+ and .gamma. methylene groups in PP are of course due to the fact that high relatively high .omega.,1 enchainment can be obtained. It is preferred that about 30 to 60 mole percent of the monomer units in PP be enchained in an .omega.,1 fashion. Using the above equation, the percent .omega.,1 enchainment for polypropylene can be calculated as:

Brief Summary Text (691):
1. They may further be irradiated with electron rays. This often improves heat resistance and/or chemical resistance, and is relatively inexpensive. Thus the molding is useful as a material required to have high heat resistance, such as a structural material, a food container material, a food wrapping material or an electric or electronic part material, particularly as an electric or electronic part material, because it is excellent in soldering resistance.

Brief Summary Text (699):
8. The polymer may be crosslinked by irradiation or chemically as by using peroxides, optionally in the presence of suitable coagents. Suitable peroxides include benzoyl peroxide, lauroyl peroxide, dicumyl peroxide, tert-butyl peroxide, tert-butylperoxybenzoate, tert-butylcumyl peroxide, tert-butylhydroperoxide, 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy) hexyne-3,1,1-bis(tert-=butylperoxyisopropyl) benzene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-bis (tert-butylperoxy)valerate, 2,2-bis(tert-butylperoxy) butane and tert-butylperoxybenzene.

Detailed Description Text (1084):
The complex [(2,4,6-MePh).sub.2 DABAn]NiBr.sub.2 was weighed (128 mg, 0.202 mmol) into a glass bottle inside a dry box. Cyclopentene was added (27.1 g, 2000 equivalents per Ni; treated with polyphosphoric acid, and distilled from Na). A solution of EtAlCl.sub.2 in hexane (6.8 mL, 1.0 M, 34 equivalents Al per Ni) was added with stirring to give a homogeneous solution. After 1 day, additional cyclopentene was added (58 g, 6200 total equivalents per Ni) to the bottle containing a heavy slurry. After 5 days, the solids were slurried with ether, collected by vacuum filtration, washed several times with ether and cyclohexane on the filter, and dried in a vacuum oven to give 36.584 g polymer (2660 turnovers/Ni). The polymer was washed with 50:50 aqueous

HCl/MeOH, followed by several washings with 50:50 H.sub.2 O/MeOH, and dried in a vacuum oven. A fine powder sample was obtained using a 60 mesh screen, and coated with 5000 ppm Irganox.RTM. 1010 by evaporating an acetone slurry and drying in a vacuum oven. The fine powder was pressed at 290.degree. C. into a transparent, pale brown, tough film. TGA (25 to 700.degree. C., 10.degree. C./min, nitrogen): T.sub.d (onset to end)=478 to 510.degree. C., 99.28% weight loss. DSC (25 to 330.degree. C., 10.degree. C./min, second heat): T.sub.g =101.degree. C., T.sub.m (onset to end)=174 to 279.degree. C., heat of fusion=25 J/g. DSC (330 to 25.degree. C., 10.degree. C./min, first cool): T.sub.c (onset to end)=247 to 142.degree. C., heat of fusion=28 J/g; T.sub.c (peak)=223.degree. C. DSC isothermal crystallizations were performed by heating samples to 330.degree. C. followed by rapid cooling to the specified temperatures, .degree. C., and measuring the exotherm half-times (min): 200 (1.55), 210 (1.57), 220 (1.43), 225 (<1.4), 230 (1.45), 240 (1.88), 245 (1.62). DSC thermal fractionation was performed by heating a sample to 330.degree. C. followed by stepwise isothermal equilibration at the specified temperatures, .degree. C., and times (hr): 290 (10), 280 (10), 270 (10), 260 (10), 250 (10), 240 (8), 230 (8), 220 (8), 210 (8), 200 (6), 190 (6), 180 (6), 170 (6), 160 (4), 150 (4), 140 (4), 130 (3), 120 (3), 110 (3). DSC (25 to 330.degree. C., 10.degree. C./min, thermal fractionation sample): T.sub.g =100.degree. C.; T.sub.m, .degree. C. (heat of fusion, J/g)=128 (0.4), 139 (0.8), 146 (1.1), 156 (1.5), 166 (1.9), 176 (2.1), 187 (2.6), 197 (3.0), 207 (3.2), 216 (3.2), 226 (3.4), 237 (3.6), 248 (3.7), 258 (2.3), 269 (1.2), 279 (0.5), 283 (0.1); total heat of fusion=34.6 J/g. DMA (-100 to 200.degree. C., 1, 2, 3, 5, 10 Hz; pressed film): modulus (-100.degree. C.)=2500 MPa, .gamma. relaxation=-67 to -70.degree. C. (activation energy=11 kcal/mol), modulus (25.degree. C.)=1600 MPa, .alpha. relaxation (T.sub.g)=109 to 110.degree. C. (activation energy=139 kcal/mol).

Detailed Description Paragraph Table (15):

33.3136 12.0398 MB.sub.1 32.9323 20.7242 MB.sub.1 32.4266 6.47794 3B.sub.5 31.9409 96.9874 3B.sub.6 .sup.+, 3EOC 31.359 15.2429 .gamma. + .gamma. + B, 3B.sub.4 31.0981 19.2981 .gamma. + .gamma. + B, 3B.sub.4 30.6606 15.8689 .gamma. + .gamma. + B, 3B.sub.4 30.2271 96.7986 .gamma. + .gamma. + B, 3B.sub.4 30.1188 54.949 .gamma. + .gamma. + B, 3B.sub.4 29.7455 307.576 .gamma. + .gamma. + B, 3B.sub.4 29.5809 36.2391 .gamma. + B, 3B.sub.4 29.3361 79.3542 .gamma. + .gamma. + B, 3B.sub.4 29.2157 23.0783 .gamma. + .gamma. + B, 3B.sub.4 27.6424 24.2024 .beta..gamma. + B, 2B.sub.2, (4B.sub.5, etc.) 27.526 29.8995 .beta..gamma. + B, 2B.sub.2, (4B.sub.5, etc.) 27.3534 23.1626 .beta..gamma. + B, 2B.sub.2, (4B.sub.5, etc.) 27.1607 70.8066 .beta..gamma. + B, 2B.sub.2, (4B.sub.5, etc.) 27.0042 109.892 .beta..gamma. + B, 2B.sub.2, (4B.sub.5, etc.) 26.5908 7.13232 .beta..gamma. + B, 2B.sub.2, (4B.sub.5, etc.) 26.3941 23.945 .beta..gamma. + B, 2B.sub.2, (4B.sub.5, etc.) 25.9446 4.45077 .beta..gamma. + B, 2B.sub.2, (4B.sub.5, etc.) 24.4034 9.52585 .beta..beta.B 24.2428 11.1161 .beta..beta.B 23.1391 21.2608 2B.sub.4 23.0227 11.2909 2B.sub.4 22.6494 103.069 2B.sub.5 .sup.+, 2EOC 20.0526 5.13224 2B.sub.3 19.7355 37.8832 1B.sub.1 19.2017 14.8043 1B.sub.1, Structure XXVII 14.4175 4.50604 1B.sub.3 13.9118 116.163 1B.sub.4 .sup.+, 1EOC 11.1986 18.5867 1B.sub.2, Structure XXVII 10.9617 32.3855 1B.sub.2

Detailed Description Paragraph Table (18):

.sup.13 C NMR data TCB, 120C, 0.05M CrAcAc Freq

ppm Intensity 39.6012 5.53532 39.4313 6.33425 MB.sub.2 38.3004 8.71403 MB.sub.3 .sup.+ 37.9446 17.7325 MB.sub.3 .sup.+ 37.2809 36.416 .alpha.B.sub.1, 3B.sub.3 36.7659 5.10586 .alpha.B.sub.1, 3B.sub.3 34.3181 56.1758 .alpha..gamma. + B 33.8243 15.6271 .alpha..gamma. + B 33.3942 8.09189 MB.sub.1 32.9854 20.3523 MB.sub.1 32.6721 4.35239 MB.sub.1 32.327 4.06305 3B.sub.5 31.9394 27.137 3B.sub.6 .sup.+, 3 EOC 31.4031 9.62823 .gamma. + .gamma. + B, 3B.sub.4 30.235 52.8404 .gamma. + .gamma. + B, 3B.sub.4 29.7518 162.791 .gamma. + .gamma. + B, 3B.sub.4 29.3164 26.506 .gamma. + .gamma. + B, 3B.sub.4 27.5695 15.4471 B.gamma. + B, 2B.sub.2 27.1341 59.1216 B.gamma. + B, 2B.sub.2 26.4811 8.58222 B.gamma. + B, 2B.sub.2 24.4475 5.93996 .beta..beta.B 23.12 5.05181 2B.sub.4 22.6369 29.7047 2B.sub.5 .sup.+, 2 EOC 20.1626 6.29481 2B.sub.3 19.7378 31.9342 1B.sub.1 19.2068 3.93019 1B.sub.1 14.2582 5.59441 1B.sub.3 13.8706 36.3938 1B.sub.4 .sup.+, 1 EOC 10.9768 9.89028 1B.sub.2

Detailed Description Paragraph Table (24):

.sup.13 C NMR data TCB, 140C, 0.05M CrAcAc Freq

ppm Intensity 47.3161 53.1767 46.9816 89.3849 46.4188 82.4488 45.84 23.1784 38.4702 12.8395 38.0985 29.2643 37.472 18.6544 37.2915 24.8559 35.3747 15.6971 34.5623 14.6353 33.3145 14.2876 32.996 12.2454 30.9464 24.2132 30.6703 57.4826 30.081 30.122 .gamma. to single branch 29.6987 29.2186 .delta..sup.+ to branch 28.3659 298.691 27.4792 33.2539 27.1235 29.7384 24.5324 9.45408 21.1554 20.0541

20.6244 110.077 19.9926 135.356 16.9342 8.67216 16.4829 8.81404 14.9962 8.38097

Detailed Description Paragraph Table (41):

.sup.13 C NMR data TCB, 140C, 0.05M CrAcAc Freq
ppm Intensity   42.6359 4.05957 .alpha..alpha. for
Me & Et.sup.+ branches 37.8987 9.10141 MB.sub.3 .sup.+ 37.2833 64.4719 .alpha.B.sub.1
36.8537 8.67514 35.5381 4.48108 34.8803 4.30359 34.5514 5.20522 34.2755 21.6482 33.2411
4.13499 MB.sub.1 32.9811 32.0944 MB.sub.1 31.9467 14.0714 3B.sub.6 .sup.+, 3EOC 30.7212
5.48503 .gamma. + .gamma. + B, 3B.sub.4 30.2597 28.5961 .gamma. + .gamma. + B, 3B.sub.4
30.143 50.4726 .gamma. + .gamma. + B, 3B.sub.4 29.7717 248 .gamma. + .gamma. + B,
3B.sub.4 29.342 17.4732 .gamma. + .gamma. + B, 3B.sub.4 27.5702 27.2867 .beta..gamma.
for 2 Me branches 27.1935 49.5612 .beta..gamma. + B, (4B.sub.5, etc.) 27.045 23.1776
23.0292 9.56673 2B.sub.4 22.6526 14.1631 2B.sub.5 .sup.+, 2EOC 20.2495 5.72164 1B.sub.1
19.7455 48.8451 1B.sub.1 13.9049 21.5008 1B.sub.4 .sup.+, 1EOC

Detailed Description Paragraph Table (42):

.sup.13 C NMR data TCB, 120C, 0.05M CrAcAc Freq
ppm Intensity   42.6041 5.16375 .alpha..alpha. for
Me & Et.sup.+ 37.851 15.9779 MB.sub.3 .sup.+ 37.5963 7.67322 37.2356 99.6734 .alpha.B1
35.4956 7.58713 34.8219 6.32649 34.6097 6.37695 34.2278 37.6181 33.3418 3.78275
MB.sub.1 32.9228 60.7999 MB.sub.1 32.2809 13.6249 31.9148 21.2367 3B6.sup.+, 3EOC
30.5886 13.8482 .gamma. + .gamma. + B, 3B.sub.4 30.4613 22.1996 .gamma. + .gamma. + B,
3B.sub.4 30.2173 48.8725 .gamma. + .gamma. + B, 3B.sub.4 30.1059 80.2189 .gamma. +
.gamma. + B, 3B.sub.4 29.7292 496 .gamma. + .gamma. + B, 3B.sub.4 29.3049 26.4277
.gamma. + .gamma. + B, 3B.sub.4 27.1511 114.228 .beta..gamma. + B.sub.1 (4B.sub.5,
etc.) 27.0025 47.5199 26.7267 20.4817 24.5623 3.32234 22.6207 36.4547 2B.sub.5 .sup.+,
2EOC 20.2176 7.99554 1B.sub.1 19.7084 70.3654 1B.sub.1 13.8677 36.1098 1B.sub.4 .sup.+,
EOC

Detailed Description Paragraph Table (49):

.sup.13 C NMR data TCB, 120C, 0.05M CrAcAc Freq
ppm Intensity   47.1728 14.6401 46.7692 9.89618
46.3285 13.3791 45.8719 7.94399 45.4684 11.1421 45.2719 7.80142 44.4754 7.11855 39.1923
29.1488 38.2791 14.2142 38.1304 18.7602 37.9074 14.9366 37.6631 15.0761 37.2809 39.5816
35.5074 8.29039 34.865 9.75536 34.5889 14.9541 34.2915 24.0579 33.2455 9.86797 32.9747
19.2516 30.6013 52.6926 30.134 55.0735 .gamma. 30.0066 25.1831 .gamma. 29.7518 144.066
.delta..sup.+ 29.3217 12.2121 3B.sub.4 28.2013 51.5842 27.9783 39.5566 27.5376 33.189
27.373 35.5457 27.1659 47.0796 27.0438 42.1247 25.6315 21.6632 terminal methine of
XXVIII 23.3589 15.3063 Methyl of XXVIII and XXIX, 2B.sub.4, 2B.sub.5 .sup.+, 2EOC
23.0722 18.4837 Methyl of XXVIII and XXIX, 2B.sub.4, 2B.sub.5 .sup.+, 2EOC 22.5306
77.0243 Methyl of XXVIII and XXIX, 2B.sub.4, 2B.sub.5 .sup.+, 2EOC 21.1129 7.78367
20.5554 26.9634 1B.sub.1 20.4386 30.3105 1B.sub.1 20.0085 22.478 1B.sub.1 19.743
46.6467 1B.sub.1 13.8812 9.03898 1B.sub.4 .sup.+, 1EOC

US Reference US Original Classification (7):
521/27

US Reference Group (7):
4329434 19820500 Kimoto et al. 521/27

Other Reference Publication (16):
N. Alberola, et al., Mechanical .gamma. and .beta. and Relaxations in Polyethylene-I.
Glass Transitions of Polyethylene, Eur. Polym. J., 28, 8, 935-948, 1992.

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L10: Entry 8 of 63   File: USPT   Aug 15, 2000

DOCUMENT-IDENTIFIER: US 6103078 A
TITLE: Methods for preparing membranes with fluid distribution passages

Detailed Description Text (17):
Various sources of radiation may be used, such as alpha rays, beta rays, gamma rays
electron beams, X-rays, and ultraviolet rays, with gamma rays and electron beams being
particularly suitable. The preferred radiation dose is 20-300 kGy.

Detailed Description Text (20):
The channel forming element is subjected to radiation grafting, typically at 200 kGy of
gamma rays in a nitrogen atmosphere, and dipped in an aqueous solution of monomer to
form a layer on the surface of the channel forming element having ion-exchange
capacity. If necessary, the monomer may then be treated to add the desired ionic
groups. The coated channel forming element, rendered ion selective through graft
polymerization, may then be positioned or affixed between the anion and cation
selective regions as discussed above.

Detailed Description Text (27):
Free-radical polymerization can be induced by irradiation of a monomer. A wide variety
of monomers can be used in the process, such as, sulfonated divinyl benzene, common
divinyl benzene or other non-conducting monomers. However, sulfonation will have to be
carried out to activate the linkage of non-conducting monomers. Sulfonation may be
accomplished by pumping fuming sulfuric acid or other sulfonating agent through the
channels.

Detailed Description Text (54):
Another method for forming membranes is by copolymerizing two different monomers
directly on the cast or mold itself. Alternatively, if the polymerization reaction is
slow enough, the monomers may be mixed in another vessel and poured onto the cast or
mold. For example, a fluorocarbon monomer reacts with styrene via gamma irradiation
initiated free-radical polymerization and is subsequently sulfonated to give sulfonic
acid pendant chains.

Detailed Description Text (55):
Grafting polystyrene onto polymeric materials (e.g. PTFE) may also be used to produce a
copolymer via gamma irradiation. Copolymer grafts may be formed by attaching an
unsaturated carboxylic acid, such as acrylic or methacrylic acid, to give carboxylic
acid pendant chains. The membrane is prepared by grafting the styrene onto the
fluorocarbon polymer using gamma irradiation and then sulfonating the grafted polymer,
for example by using fuming sulfuric acid (H.sub.2 SO.sub.4 SO.sub.3), chlorosulfonic
acid, or grafting an unsaturated carboxylic acid onto the fluorocarbon polymer using
gamma irradiation. The gamma irradiation of the fluorocarbon polymer forms free radical
sites, which are then available for reaction with an unsaturated monomer, such as
styrene. Again, this was discussed earlier. The electrolytic resistance of the ion
exchange membrane is related to the percentage of styrene grafted thereon. When
subsequently sulfonated, the electrolytic resistance decreases as the percent graft
increases. In general, the useful range of the percent graft is from 10 to 50 percent,
more preferably 10 to 20 percent. The membrane to be modified is generally made from a
polytetrafluoroethylene or an ethylene-propylene copolymer base film of the desired
thickness which is grafted with styrene via gamma irradiation, using a cobalt-60
source.

Current US Cross Reference Classification (5):
521/27

Issued US Cross Reference Classification (5):
521/27

Field of Search Class/SubClass (1):
521/27

US Reference US Original Classification (11):
521/27

US Reference US Original Classification (12):
521/27

US Reference Group (11):
5849167 19981200 Posar 521/27

US Reference Group (12):
5958616 19990900 Salinas et al. 521/27

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L10: Entry 15 of 63   File: USPT   Jul 1, 1997

DOCUMENT-IDENTIFIER: US 5643968 A
TITLE: Process for producing ion exchange membranes, and the ion exchange membranes produced thereby

Brief Summary Text (37):
Various post-treatments could be applied to the membranes to alter or stabilize the properties. These include, but are not limited to, reaction with compounds that react with the functional groups to induce crosslinking, irradiation, for example by electron beam, to induce crosslinking and contact with electrolyte solutions of various concentrations, generally at elevated temperature. Depending on the starting membrane these treatments can either reduce porosity or increase the water content.

Issued US Original Classification (1):
521/27

Current US Original Classification (1):
521/27

Field of Search Class/SubClass (1):
521/27

US Reference US Original Classification (1):
521/27

US Reference US Original Classification (2):
521/27

US Reference US Original Classification (20):
521/27

US Reference Group (1):
3247133 19660400 Chen 521/27

US Reference Group (2):
3258435 19660600 Imoto et al. 521/27

US Reference Group (20):
4895634 19900100 Giuffre et al. 521/27

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L10: Entry 23 of 63   File: USPT   Jul 19, 1994

DOCUMENT-IDENTIFIER: US 5330626 A
TITLE: Irradiation of polymeric ion exchange membranes to increase water absorption

Abstract Text (1):
The present invention is a process for modifying a fluorinated ion exchange membrane by irradiation of the membrane with a sufficient dose of non-spark-producing radiation to increase water absorption and/or ionic conductivity of the membrane. The membranes are particularly useful in fuel cells and chloralkali cells.

Brief Summary Text (2):
This invention relates to fluorinated ion exchange polymer films and membranes which are used in electrochemical cells, particularly chloralkali cells and fuel cells. It particularly relates to the irradiation of such films or membranes to increase water absorption and ionic conductivity.

Brief Summary Text (7):
It is known that the irradiation of a fluorinated ion exchange membrane may improve cell voltage. U.S. Pat. No. 5,128,014 (Banerjee) discloses and claims a process for irradiating a fluorinated ion exchange membrane.

Brief Summary Text (8):
U.S. Pat. No. 4,439,292 (Klotz et al.) also teaches irradiation of perfluorinated polymeric membranes in the presence of a monomer in order to facilitate cross-linking of the membrane to lower voltage in an electrolytic cell. U.S. Pat. No. 4,439,292 reduced cell voltage by treating fluorinated carboxyl membranes with corona discharge, a process in which an electrical discharge or spark is passed from one electrode to another through a gas and through the sample to be treated. Klotz et al. found that heating damaged the membrane. They chose to keep the temperature below 80.degree. C., preferably below +22.degree. C., and most preferably below -20.degree. C. To prevent heat damage, Klotz et al. exposed the sample to corona discharge 1000-5000 times, with cooling between exposures. Clearly, the need to use thousands of exposures is a severe limitation to the usefulness of this process.

Brief Summary Text (10):
In the present invention, a fluorinated ion exchange membrane is irradiated with a non-spark-producing ionizing radiation. The membrane is irradiated with a dose of radiation sufficient enough to provide improved water absorption and/or ionic conductivity. The tensile properties of the membrane are not significantly altered by irradiation.

Drawing Description Text (2):
FIGS. 1-4 show graphs of ionic conductivity vs. temperature for fluorinated ion exchange membranes exposed to irradiation levels of 0, 1, 5 and 10 megarads, respectively.

Drawing Description Text (3):
FIGS. 5-7 show graphs of water absorption vs. radiation dosage for various fluorinated ion exchange membranes exposed to irradiation levels of 0-10 mrad.

Drawing Description Text (4):
FIG. 8 is a graph showing water absorption vs. radiation dosage for a membrane which was irradiated in the sulfonic acid salt (SO.sub.3.sup.- K.sup.+) form and then was rehydrolyzed.

Drawing Description Text (5):

FIGS. 9 and 10 are graphs showing tensile stress and tensile modulus, respectively, of irradiated membranes.

Detailed Description Text (2):
The process for modifying a fluorinated ion exchange membrane involves irradiating the membrane with a non-spark-producing ionizing radiation. The sources of this type of radiation include but are not limited to (1) gamma sources, such as Co-60 and Cs-137, (2) beta sources (often referred to as electron beam accelerators or linear accelerators, and (3) x-rays. All ionizing radiation produces free radicals in the absorbing medium (the material being irradiated). The behavior of the free radicals produced is determined by the nature of the absorbing medium. The main difference between these three sources is the manner in which the radiation travels through the material being irradiated.

Detailed Description Text (3):
The most common sources of gamma radiation are Co-60 and Cs-137. Co-60 is made by pre-forming non-radioactive Co into rods or bars, then subjecting them to a neutron source such as the neutrons produced in a nuclear power plant.

Detailed Description Text (4):
Gamma radiation is emitted in a complete sphere, requiring the target material to completely surround the source if all of the irradiation is to be utilized. Gamma radiation is absorbed on a logarithmic basis as it travels in a material. In order to get a more uniform dose in the material, double sided exposure may be used, but is not necessary with a relatively thin material such as a chloralkali membrane. Gamma rays have a major advantage, penetration. This is not important in irradiating thin membranes.

Detailed Description Text (6):
X-rays are produced when high energy electrons are used to bombard metals. The efficiency of the x-ray source is determined by the molecular or atomic weight of the target and by the energy (accelerating voltage) of the electrons. The higher the molecular weight of the target material, the greater the efficiency. The efficiency is also proportional to the accelerating voltage. The penetration characteristics of x-rays are 5-20% greater than those of gamma rays.

Detailed Description Text (7):
The source of beta radiation is an electron beam accelerator. Electrons can be accelerated by (1) high DC voltages, (2) electric pulses, (3) magnetic pulses, or (4) a combination of these three. COCKCROFT-WALTON, isolated core, resonant transformer, DYNAMITRON (high voltage generated by a set of cascade rectifiers coupled to an oscillator), KLYSTRON (evacuated electron beam generator) and linacs are some of the names given to the techniques of producing high voltages. Absorption of high energy electrons in material is such that 90% of the beam energy may be used with a maximum to minimum dose ratio of 1.4 using a single pass under the beam.

Detailed Description Text (8):
The main advantages of the electron beam accelerators are the (1) high power and high throughput, (2) relatively low unit cost, (3), high dose rate, and (4) intrinsic safety. In addition, since electron accelerators may be turned off, the facilities do not have to be operated continuously. The main disadvantage of electron beam accelerators is the relatively small penetration of the electrons, about 2.1 cm in water for a 5 megarad source. This is not a significant disadvantage for irradiation of membranes, which are thin. Therefore, electron beam accelerators are the preferred source of ionizing radiation for this invention.

Detailed Description Text (10):
In the irradiation process, the membrane is exposed to irradiation for a sufficient time and at a sufficient dose rate to cause an increase in water absorption and/or an increase in ionic conductivity. The total dosage should be at least 0.1 megarads, preferably about 5.0-10.0 megarads, most preferably 5.0 megarads. Doses higher than 10 megarads are possible but, as can be seen in the Examples and the Figures, does not provide further improvement in the properties of the membrane.

Detailed Description Text (12):
It is believed that the increased water absorption of irradiated membranes having sulfonyl groups is due to the presence of carboxylate groups after irradiation. In particular, it is believed that irradiation generates acid-type carbonyl containing functional groups which are converted to carboxylate groups on further hydrolysis. The

carboxylate groups are ionic and tend to absorb more water.

Detailed Description Text (13):
The total dosage of radiation is a function of the time of each exposure, the dose rate, and the number of exposures. Preferably the number of exposures should be low, most preferably one. The dose rate will depend on the type of radiation used, the device used to generate the radiation, and the energy input to the source of radiation. For a given dose rate, the time of exposure can be varied to provide the preferred total dosage. A preferred way of controlling the time of exposure is to vary the speed of a conveyor system carrying the membrane through the irradiation zone. The membranes may also be irradiated in a so-called "shield pack" or a package or container which is not effected by the radiation. Such irradiation may be performed under ambient atmosphere, under vacuum or otherwise. Such a package or container prevents damage to the membrane from excessive handling.

Detailed Description Text (14):
The irradiated membrane is broadly useful in the chloralkali industry for providing a more efficient and economical operation of chloralkali cells. The irradiated membrane is also broadly useful in the fuel cell industry, chemical separations, facilitated transport and the like.

Detailed Description Text (16):
The membrane used in the electrolytic cells according to the process of this invention may consist of two or more layers, where preferably the one layer in contact with the anolyte has pendant sulfonyl groups. For membranes having more than one polymer layer, it is possible to irradiate the layers independently and then laminate the layers to form the membrane or the multilayer membrane may be irradiated after the layers have been laminated.

Detailed Description Text (20):
The sulfonyl polymers and carboxylic polymers described herein are not limiting and the irradiation process is useful for a wide range of fluorinated ion exchange membranes. The polymers herein and the corresponding methods of polymerization are well known and described in the prior art.

Detailed Description Text (39):
The hydrolyzed film was irradiated in a vacuum with an electron beam at Irradiation Industries, Inc., Gaithersburg, Md. The equipment used for irradiation was a 3.0 million electron volt, 25 milliampere Dynamitron manufactured by Radiation Dynamics, Inc. The irradiation dosage for the hydrolyzed film was chosen to be 0, 1, 5, 10, or 40 megarads.

Detailed Description Text (40):
The irradiated membrane pieces were washed in deionized water. The pieces were dried in a vacuum oven at 90.degree. C. (with a nitrogen purge) overnight. The dry pieces were removed from the oven and weighed. The pieces were then put in a beaker containing 80.degree. C. deionized water for one hour. The membrane pieces were then quickly dried on a towel and weighed.

Detailed Description Text (44):
FIGS. 1, 2, 3 and 4 show the ionic conductivity, cell temperature and frequency for membranes irradiated with doses of 0, 1, 5 and 10 megarads, respectively.

Detailed Description Text (48):
The films were irradiated as in Example 1 at radiation doses of 0-10 mrads. The irradiated films were then washed and dried as in Example 1. The 5 mil SO.sub.2 F form film was then hydrolyzed as in Example 1.

Detailed Description Text (50):
FIG. 5 shows the water absorption vs. radiation dosage for both 5 mil ion exchange films in the K.sup.+ form. FIG. 6 shows the water absorption vs. radiation dosage for the same two 5 mil ion exchange films after they have been converted to the H.sup.+ form by treating in HCl for one hour at 85.degree. C. It is apparent that the irradiated membranes have significantly increased water absorption, especially when irradiated int he sulfonyl fluoride form at about 5 mrad.

Detailed Description Text (51):
FIG. 7 shows the water absorption for the 7 mil membrane (NAFION.RTM. N117), which was irradiated in the hydrolyzed form (SO.sub.3.sup.- K.sup.+). This membrane also exhibits

increased water absorption.

Detailed Description Text (52):
The 5 mil film that was irradiated in the SO.sub.3.sup.- K.sup.+ form was again rehydrolyzed using the same procedure as in Example 1. The water absorption of this rehydrolyzed film is shown in FIG. 8. In this Figure, it is seen that on rehydrolysis the water absorption increases even more than the water absorption of the same film before rehydrolysis.

Detailed Description Text (54):
The tensile strength of the two 5 mil films from Example 2 was measured. Tensile stress at 10% elongation and tensile modulus were tested by ASTM D882. FIGS. 9 and 10 show tensile stress and tensile modulus of the membranes at different levels of radiation. The tensile properties of the membrane do not change significantly after irradiation.

Current US Cross Reference Classification (7):
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Issued US Cross Reference Classification (2):
521/27

Field of Search Class/SubClass (3):
521/27

US Reference US Original Classification (15):
521/27

US Reference Group (15):
4602045 19860700 Markus et al. 521/27

CLAIMS:

1. A process for modifying a fluorinated ion exchange membrane comprising irradiating said membrane, in an environment substantially free of a monomer which would graft polymerize with components of said membrane, with a non-spark-producing ionizing electron beam radiation with a dose of about 1-10 megarads.

3. The process of claim 1 wherein the membrane is irradiated in its unhydrolyzed form.

4. The process of claim 1 wherein the membrane is irradiated in its hydrolyzed form.

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L16: Entry 4 of 5   File: USPT   Sep 25, 1979

DOCUMENT-IDENTIFIER: US 4169023 A
TITLE: Electrolytic diaphragms, and method of electrolysis using the same

Abstract Text (1):
An electrolytic diaphragm consisting essentially of a main layer composed of a
polymeric membranous material uniformly containing cation exchange groups and fluorine
atoms chemically bonded thereto and a secondary layer having a smaller thickness than
said main layer and composed of at least one of an electrically neutral layer and a
layer containing an anion exchange group, said secondary layer being in intimate
contact with said main layer at at least one surface layer portion or interior of said
main layer. A method for electrolyzing alkali salts, using aforesaid electrolytic
diaphragm.

Brief Summary Text (9):
The present invention thus provides an electrolytic diaphragm consisting essentially of
a main layer composed of a polymeric membranous substance containing a cation exchange
group and a fluorine atom uniformly and chemically bonded thereto and a secondary layer
having a smaller thickness than the main layer and composed of an electrically neutral
layer and/or a layer containing an anion exchange group, said main layer being in
intimate contact with said secondary layer.

Brief Summary Text (13):
Generally, in cation exchange resin membranes, hydroxyl ions far more readily enter the
membranes than other anions, and therefore, the concentration of bases in the membranes
becomes high. Thus, the amount of the bases to be diffused into the anode compartment
owing to a concentration gradient is much larger than those of the salts and acids. In
the case of electrolysis, electrophoretic migration of the hydroxyl ions into the anode
compartment occurs under the incluence of an electric field, in addition to their
diffusion caused by this concentration gradient. This cause a marked reduction in the
current efficiency of forming bases. This is also true in the case of membranes made of
fluorine-containing cation exchange resins. However, if a thin neutral layer and/or a
thin layer containing anion exchange groups is present in the cation exchange resin
membrane as in the electrolytic diaphragms of this invention, the diffusion of the
hydroxyl ions into the cation exchange resin membrane is considerably impeded by a
sieving effect of the hydroxyl ions based on the presence of the compact secondary
layer (in the case of the neutral layer), or both by the above sieving effect and a
Donnan exclusion effect of alkali metal ions (in the case of the layer containing anion
exchange groups). Consequently, the amounts of bases diffused and electrically
migrating through the membrane are markedly reduced, and the current efficiency for
forming bases increases greatly.

Brief Summary Text (14):
The term "electrically neutral layer" (to be sometimes referred to hereinbelow as a
neutral layer), as used in the present application, denotes both (1) a layer containing
no ion exchange group, and (2) a layer in which cation exchange groups and anion
exchange groups are present in substantially equal amounts as ion equivalents and which
is substantially electrically neutral as a result of the neutralisation of the two
types of ion exchange groups with each other. In the electrolytic diaphragms of this
invention, the use of a neutral layer of the type (1) above is preferred.

Brief Summary Text (15):
The characteristic feature of the electrolytic diaphragm of this invention is that a
main layer of a membranous polymeric substance uniformly containing fluorine atoms and
cation exchange groups chemically bonded to each other (may sometimes be referred to as
a cation exchange resin layer) and a secondary layer composed of a layer having a

smaller thickness than the main layer and containing anion exchange groups (may
sometimes be referred to as an anion exchange substance layer) or a neutral layer
having a smaller thickness than the main layer or both are present in intimate contact
with each other. The relative positions of the main layer and the secondary layer are
not particularly critical. Thus, the secondary layer may be formed on one or both
surfaces of the membranous cation exchange resin layer, or at least one secondary layer
may be sandwiched between the cation exchange resin layers.

Brief Summary Text (32):
Examples of the anion exchange groups present in the secondary layer in accordance with
this invention are primary, secondary and tertiary amines, or general onium salt groups
such as quaternary ammonium salts, tertiary sulfoniums, quaternary phosphoniums,
stiboniums and arsoniums, and metal chelates having a positive charge such as a
cobalticinium.

Brief Summary Text (44):
One embodiment of the above method involves the formation of a thin neutral layer by
matrix polymerization. For example, when a cation exchange group such as sulfonic,
carboxylic or phosphoric groups of a cation exchange resin layer having bonded thereto
fluorine atoms is converted to an acid type, this acid-type cation exchange resin
membrane itself is a kind of solid acid and acts as an acid catalyst. Accordingly, by
adhering a substance polymerizable in the presence of this acid catalyst, such as
4-vinylpyridine, to one or both surfaces of the cation exchange resin layer, and
polymerizing it, a neutral layer can be formed. Sometimes, depending upon the state of
distribution of the cation exchange group in the cation exchange resin layer, the
excess of such a polymerizable substance polymerizes to form a thin anion exchangeable
layer instead of the neutral layer. If desired, such an anion exchangeable thin layer
can be converted to a neutral layer by suitable means such as oxidative decomposition.

Brief Summary Text (51):
When it is desired to form layer having an anion exchange group as the secondary layer
in intimate contact with the surface layer of the cation exchange resin layer or its
base membrane, the same methods as shown in (A), (B), (C), (D), (E) and (F) above can
be used except that a substance having anion exchangeability is used instead of the
neutral substance. One example of such methods involves using a substance containing at
least two anion exchange groups (such as ethylenediamine, triethylenetetramine,
polyethyleneimine or piperazine) as a treating substance, chemically bonding the
substance to the anion exchange resin layer or its base membrane using one anion
exchange group, and utilizing the other anion exchange groups effective as anion
exchange groups in the secondary layer.

Brief Summary Text (57):
When electrolysis is carried out over long periods of time using the electrolytic
diaphragms of this invention, the current efficiency sometimes tends to decrease
somewhat with the passage of time. This tendency is considered to be due to the
stripping or decomposition of the secondary layer from the surface of the cation
exchange resin layer after use for long periods of time. In such a case, a soluble
cationic substance, such as a fluorinated cationic surface active agents (for example,
FLUORAD FC-134, a registered trademark for a product of Sumitomo-3M) or cationic
polyelectrolytes, (for example polyethyleneimine) is added continuously or
intermittently to the anodic solution; as a result, the cationic substance added
migrates to the cathodic side by the influence of an electric field to adhere firmly to
the surface of the electrolytic diaphragm and to form a fresh secondary layer having
anion exchange groups. This enables the lowered current efficiency to increase again.
The above procedure is also available to form a secondary layer containing anion
exchange groups on a cation exchange resin membrane consisting only of a cation
exchange resin layer specified in this invention in intimate contact with each other.
When this procedure is used, the above-mentioned cationic substance is added to the
anodic solution while electrolysis is carried out using the cation exchange resin
membrane containing no secondary layer.

Detailed Description Text (31):
Both surface layers of this cation exchange membrane were coated with a mixture
consisting of 90 parts of benzene and 10 parts of polystyrene having a molecular weight
of 20,000, and after driving off the benzene, the membrane was subjected to irradiation
at room temperature at a dose of $2.times.10.sup.6$ rads from a .gamma.-ray irradiation
source of Co.sup.60 thereby to graft copolymerize the polystyrene onto the surfaces of
the cation exchange membrane while partially crosslinking the polystyrene. The
resulting neutral layer had a thickness of about 10 microns.

Detailed Description Text (75):
Using the cation exchange membrane of this invention prepared in Example 1 and the
anion exchange membrane disclosed in Japanese Patent Application No. 63856/73, salt
cake was electrolyzed.

Detailed Description Text (76):
The above anion exchange membrane was prepared by coating a woven cloth of
polypropylene with a solution of a styrene/butadiene copolymer and dicumyl peroxide in
chloromethyl styrene and divinyl benzene, and while covering both surfaces with a
Cellophane sheet, heat polymerized to form a membranous material. The membranous
material obtained was treated with a mixture of acetone, water and trimethylamine. The
surface layer portion of the resulting strongly basic anion exchange membrane was
impregnated with 1,8-dihydroxy-3,5-dinaphthalenesulfonic acid, followed by condensation
with formaldehyde. This anion exchange membrane exhibited markedly reduced diffusion
and leakage of acid.

Detailed Description Text (77):
An anode, the anion exchange membrane, the cation exchange membrane of this invention,
and a cathode were arranged in this sequence to build a three-compartment electrolytic
cell with an effective membrane area of 1 dm.sup.2. Using this cell, 4.0 N sodium
sulfate (Na.sub.2 SO.sub.4) was flowed into an intermediate compartment defined by the
anion exchange membrane and the cation exchange membrane, and 4.0 N sulfuric acid was
obtained from the anode compartment while 4.0 N sodium hydroxide was obtained from the
cathode compartment. The current efficiency for obtaining sulfuric acid was 92%, and
the concentration of sodium sulfate in the sulfuric acid was 0.0003 N. From the cathode
compartment, 4.0 N sodium hydroxide could be obtained with a current efficiency of 93%,
and the concentration of sodium sulfate in the sodium hydroxide was 0.0002 N.

Detailed Description Text (78):
When the above procedure was repeated using the same anion exchange membrane as above
but a cation exchange membrane (NAFION XR-480) not treated in accordance with this
invention, the current efficiency for forming 4.0 N sulfuric acid was 85%, and the
concentration of sodium sulfate in the sulfuric acid was 0.0004 N. The current
efficiency for obtaining 4.0 N sodium hydroxide was 82%, and the concentration of
sodium sulfate in the sodium hydroxide was 0.003 N. The current density was 20
A/dm.sup.3.

Detailed Description Text (91):
A polymeric compound of the formula ##STR5## (1, m and n are integers) was melted, and
formed into a sheet having a thickness of 0.2 mm. The resulting sheet was immersed in
ethylene diamine at 60.degree. C. for 24 hours to obtain a membrane containing anion
exchange groups on both surfaces through a sulfonamide bond. Two of such membrane were
laminated and melt adhered to form a sheet having a thickness of 0.4 mm. Separately,
two of the above polymer sheets not treated in the above manner were melt adhered to
form a sheet having a thickness of 0.4 mm. Cation exchange groups were introduced into
these laminated sheets under the same conditions as in Example 3.

Detailed Description Text (94):
The base membrane used in Example 5 was immersed in each of the reactant baths shown in
Table 16, and reacted at 80.degree. C. for 24 hours thereby to form a secondary layer
containing anion exchange groups on the surface of the membrane. The membrane was then
treated with an aqueous solution of sodium hydroxide to introduce cation exchange
groups into the interior of the membrane. Using each of the resulting membranes, a
saturated aqueous solution of sodium chloride as an anodic solution was electrolyzed at
80.degree. C. with a current density of 20 A/dm.sup.2 in a two-compartment cell having
a membrane area of 1 dm.sup.2, and 5 N sodium hydroxide was obtained from the cathode
compartment. The properties of the membranes and the results of electrolysis are shown
in Table 16.

CLAIMS:

1. An electrolytic diaphragm consisting essentially of a main layer composed of a
polymeric membranous material uniformly containing cation exchange groups and at least
one fluorine atom chemically bonded to a carbon atom of the polymer backbone and a
secondary layer having a smaller thickness than said main layer and composed of at
least one compact ion permeable, liquid impermeable and hydroxyl ion sieving layer
containing an anion exchange group, said secondary layer being in intimate contact with
said main layer and impeding the diffusion of hydroxyl ions into the main layer.